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Characterization of silica gel prepared by using sol-gel process

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Abstract

We studied the preparation of silica gels from sodium silicate solution mixed with hydrochloric acid by sol-gel process. The obtained gel is washed with water to obtain a "hydrogel". The immersion of the last one in alcohol, gives an "alcogel". A Hoke D6 experimental design was followed in order to limit the number of tests. pH and the silica concentration represent the most significant factors which control the obtaining of a significant specific surface and thus a great capacity of adsorption. A second order polynomial model was adopted in order to represent the results in the form of three-dimensional surfaces. These results are also topographically illustrated as isoresponses lines. The results showed that the pH effect is more significant than the silica concentration one. We obtained gels with great microporosity and presenting specific surfaces of 657 m2.g-1 when pH is equal to 2. The prepared gel without alcohol presents interesting characteristics for a potential industrial use since its production cost is lowest and has a high specific surface.

PACS: Type pacs here, separated by semicolons ;

Keywords: Silica gel, Adsorption, Experimental design, Modelling, Optimization.

1. INTRODUCTION

The preparation of silica gels as adsorbent was the object of several works [1-2]. A gel can be defined as a solid occupying the totality of the liquid volume which gave him birth, whereas a precipitate is a solid formed from a dense aggregates dispersed in a solution [1]. The gel formation is obtained after destabilization of the silico-alkaline solutions by acid addition [3].

The objective of this work consists to prepare and characterize a silica gel, according to sol-gel process [2], from Tunisian sand. The preparation of silica gel depends on many factors. A preliminary study allows determining the most significant factors and their variation fields. Three parameters are retained: the precursor concentration (sodium silicate), pH and the additives (methanol, ethanol). Specific surface area was selected as response function allowing obtaining gel with interesting porous texture.

A Hoke D6 experiment matrix is used to represent the responses of parameters in all studied experimental fields [4-6]. The choice of the Hoke D6 experiment matrix is justified by several advantages: (i) the possibility of presenting a uniform distribution of the experimental points in studied space, (ii) the capacity to explore all the

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fields, (iii) the utility to interpolate the responses, (iv) the possibility of adding new factors without deteriorating the quality of the matrix.

2. EXPERIMENTAL

2. 1. Material

The used sand comes from a layer located in the area of Feriana (Kasserine) in Tunisia. Its chemical composition is determined by atomic absorption spectrometry "Polarized Zeeman" (Shimazu Z-6100), after attack of the rock by hydrochloric acid. Table 1 recapitulates obtained results:

Table 1. Sand composition.

Element	SiO_2	Fe_2O_3	MgO	Al_2O_3	K_2O	Na_2O	CaO	PF	total
(%) **mass**	94.51	2.69	0.049	0.63	0.55	0.023	0.005	1.69	100.147

Loss on ignition is determined by gravimetry, after calcinations of material until 1000°C. The particular choice of this material dependent on its chemical composition rich in SiO_2 .

The sand is put in suspension in a soda solution; the attack is done during two hours, at a temperature of 220°C and a pressure of about 27 to 32 bars. The formation reaction of sodium silicate is the following [7]:

$$n\,SiO_2 + 2\,(NaOH, x\,H_2O) \rightarrow n\,SiO_2, Na_2O, y\,H_2O \quad (1)$$

In this work, the inorganic precursor used is the sodium metasilicate (Na_2SiO_3); n is the ratio $\frac{SiO_2}{Na_2O}$ equal to 1 [3].

2.2. Sol-gel process

The sol-gel process is the transformation allowing the passage of the sol to the gel. The starting solution is called sol: it is a suspension of solid particles in a liquid [2]. By polymerization, we obtain a network which is a solid phase in a liquid one. When this network reaches macroscopic dimensions we obtained a gel [8,9].The used chemical reagents for the gel synthesis are mainly: precursor, solvent, water, catalyst and additives. The gel characteristics will depend on the nature of these compounds [2].

Silica gels are prepared from the reaction between hydrochloric acid and sodium metasilicate solution (Na_2SiO_3). It is a polymerization followed by a condensation of silicic acid [$Si(OH)_4$] [3]. Condensation can continue during several months, the duration depends on temperature and pH; we obtain a "hydrogel" [10, 11]. Water plays a double role: it is solvent and hydrolysis reagent at the same time; it is abundant in the solution and has a great capacity of solubility for the used precursor [12].

$$Na_2SiO_3 \xrightarrow{H_3O^+} \underset{\text{acid silicic}}{[Si(OH)_4]} \xrightarrow{-H_2O} \underset{\text{acid disilicic}}{[(HO)_3SiOSi(OH)_3]} \xrightarrow{-n\,H_2O} \text{"silica gel"} \quad (2)$$

As the network grows it becomes more rigid. It contracts, by expelling the liquid present inside the pores, trapped during the polymerization; it is synaeresis phenomenon [2]. Hydrogel becomes less porous, harder and cannot be compressed, therefore more ready to resist on this collapse. Moreover, the pores became smaller, thus the tension in the liquid increased [13]. Hydrogel obtained is fragmented then washed by filtration on Buchner with distilled water until complete elimination of chloride ions formed simultaneously. Water impregnating the gel can be replaced by an alcohol (methanol or ethanol) in order to improve the quality of gel prepared. It is used, firstly, to obtain size uniformity of pores which gives rigidity to the gel, secondly, to facilitate the non-destructive drying of the gel, we obtains an "alcogel".

Drying is an important step which modifies the gel characteristics; it is composed of two steps [14]. During the first step, the pores are emptied; the capillarity gradient induces the liquid flow along the pores wall, towards external surface where it evaporates. At the interior, the pores are still filled with liquid, while the air enters the most external pores, which can cause the opacity of gel. The pressure capillary gradient decreases gradually, the flow is

increasingly slower then stops. The remaining liquid can then leaves the gel only in gas form, with vapour diffusion towards surface; it is the second step.

Generally, after a drying at 50°C, porous gel contains a small quantity of liquid trapped in the pores (not evaporated solvents, absorbed water).

2.3. Silica gel characterization

Specific surface area (S) of an adsorbent is a significant characteristic: it is the surface offered by the pores of one gram of solid ($m^2.g^{-1}$). It is the sum of external and internal surfaces, i.e. the geometrical surface of the particles and the surface developed by the walls of the pores.

The specific surface areas of the silica gel samples were measured from the isotherm of adsorption-desorption of liquid nitrogen at its normal boiling point (77.4 K) according to the BET method.

2.4. Identification of silica gel production parameters

The silica gel production depends on several parameters. The influences of gelling and ageing times of gel were studied in order to optimize the production of silica gel [2].

The pH has a significant role in the reactions evolutions. For acid pH, the hydrolysis is accelerated, rather for basic pH, the condensation is favoured. Acid or basic catalysis does not influence the kinetics of hydrolysis and condensation reactions, but also modifies the morphology of obtained products. In acid medium, little ramified species are formed leading to linear polymers; while in basic medium, much ramified species are formed leading to dense colloidal particles [1].

The influence of sodium metasilicate concentration has been studied when silica quantity vary between 10 and 30 $g.L^{-1}$ in 2M hydrochloric acid medium.

A preliminary study shows that for concentrations lower than 10 $g.L^{-1}$, the gelling time is very long, while for concentrations higher than 40 $g.L^{-1}$ the precipitation was instantaneous. The gelation can take several days, even several weeks for $pH \leq 2$, whereas for basic solutions, the gelling is instantaneous. The gelling time is a parameter which depends on pH and metasilicate solution concentration.

In this work, the influence of these two parameters was studied: the pH (Z_1) and SiO_2 (Z_1) concentration in order to determine the optimal operating conditions needed to produce a preferment gel. The limits fields of these factors are presented in Table 2.

Table 2. Selected experimental field.

Parameter	**Unit**	**Level (-1)**	**Level (0)**	**Level (+1)**
pH	(-)	2	5	8
SiO_2 concentration	($g.L^{-1}$)	10	20	30

Alcohol is a factor which improves the quality of prepared silica gel; that is why we chose it as an influential factor in the research of the silica gel preparation conditions. Three cases are studied: two alcoholic solutions one with methanol and the other with ethanol, the third case is a solution without alcohol.

2.5. Experimental design methodology

Response surface methodology (RSM), a combination of mathematical and statistical techniques, was useful for modelling and analysing of problems. The response was influenced by several variables. The objective of this methodology was to optimise this response. For each response, the coefficients of the postulated model were calculated on the basis of the experimental responses by least squares regression using the NEMROD software (New Efficient Methodology for Research using Optimal Design). In this work we chose a Hoke D6 experimental design with three levels (table 2). The Hoke D6 matrix consists of N experiments with $N = K^2 + 2K + 1$, where K is the number of variables studied. In this case, $K = 2$ and, therefore, the matrix was comprised of nine experiments with one in the centre [4-6]. The original variables Z_1 and Z_2 have equations with different dimensions. It is thus

impossible to compare their effects in their own units for the studied property. To mitigate this disadvantage, coded variables, x_j, are used. They are without dimensions taking levels -1, 0 and +1 when the original variables take inferior, means and superior levels. The use of coded variables facilitates the calculations and allows considering discrete qualitative variables. We applied this experimental design for the three cases quoted before (methanol, ethanol and without alcohol). The establishment of cognitive model of silica gel preparation requires a detailed knowledge of kinetics which adopted experimental methodology allows it very partially. We thus chose a statistical model representation. It is a second degree polynomial equation connecting the results of the tests, Y, with the preparation parameters x_j, in dimensionless form.

As in fitting any linear model, analysis of the residuals from a regression model was necessary to determine the adequacy of the least squares fit. This could be done by studying of the normal probability plot, a plot of residuals versus fitted values. This plot must indicate the absence of any serious violation of the normality assumption.

After validation of the obtained models, a visual interpretation of the functional relations was made by using different projections and graphic illustrations of the shape of the response surfaces.

3. RESULTS AND DISCUSSIONS

The studied experimental response is the specific surface (Y), are given in Table 3.

Table 3. BET experimental specific surface area.

No. Exp.	pH	Silica concentration	Specific surface area		
			Methanol	Ethanol	Without alcool
	(-)	($g.L^{-1}$)	($m^2.g^{-1}$)	($m^2.g^{-1}$)	($m^2.g^{-1}$)
1	2	10	463.50	**619.00**	**657.60**
2	8	20	87.58	92.32	104.10
3	5	30	253.70	232.10	228.40
4	8	10	124.90	128.00	124.80
5	2	30	**635.20**	594.00	279.20
6	8	30	71.58	92.29	70.04
7	2	20	556.40	522.50	558.80
8	5	10	391.20	391.50	539.70
9	5	20	212.60	122.30	418.10

The specific surfaces values measured for each solvent were used to compute the model coefficients by using the least squares method. This allowed us to write the two resulting estimated models:

Methanol $\hat{Y}_1 = 260.620 - 228.507\ X_1 - 3.187\ X_2 + 37.360\ X_1^2 + 37.820\ X_2^2 - 56.255\ X_1X_2$ (3)

Ethanol $\hat{Y}_2 = 183.894 - 237.148\ X_1 - 36.685\ X_2 + 92.718\ X_1^2 + 97.108\ X_2^2 - 2.677\ X_1X_2$ (4)

Without alcool $\hat{Y}_3 = 424.540 - 199.443\ X_1 - 124.077\ X_2 - 96.310\ X_1^2 - 43.710\ X_2^2 + 80.910\ X_1X_2$ (5)

3.1. Analysis of variance

Results of analysis of variance were summarized in Table 4. They indicated that the three regressions were significant at the probability level of 95 % to 99 %. In addition, the normal probability plots of the obtained residuals (fig. 1, 2 and 3) did not reveal anything particularly troublesome. Moreover the R^2 for the three models computed as:

$$R^2 = \frac{\text{Sum of squares attributed to the regression}}{\text{Total Sum of squares}} \quad (6)$$

Table 4. Analysis of variance.

Response	Source	Sum of squares	Degrees freedom	Mean square	Rapport	Signif	R^2
$\hat{Y}_1$	Regression	3.31663×10^5	5	6.63327×10^4	10.9409	3,89 *	0.948
	Residues	1.81886×10^4	3	6.06284×10^3			
	Total	3.49852×10^5	8				
$\hat{Y}_2$	Regression	3.81593×10^5	5	7.63186×10^4	14.7269	2,57 *	0.961
	Residues	1.55468×10^4	3	5.18227×10^3			
	Total	3.97140×10^5	8				
$\hat{Y}_3$	Regression	3.79594×10^5	5	7.59188×10^4	42.0192	0,553 **	0.986
	Residues	5.42029×10^3	3	1.80676×10^3			
	Total	3.85014×10^5	8				

* Significant with 95% confidence degree
** Significant with 99 % confidence degree

Per response, a distribution plot of the residuals versus the predicted values of the response and a normal probability plot of residuals were created (Fig. 1, 2 and 3). The analysis shows the absence of any serious violation of the normality assumption. Subsequently, the analysis of variance was performed. Analysis of variance is an important statistical analysis and diagnostic tool which helps us to determine the statistical significance of regression.

(a) residual versus responses (b) normal probability plot of residuals

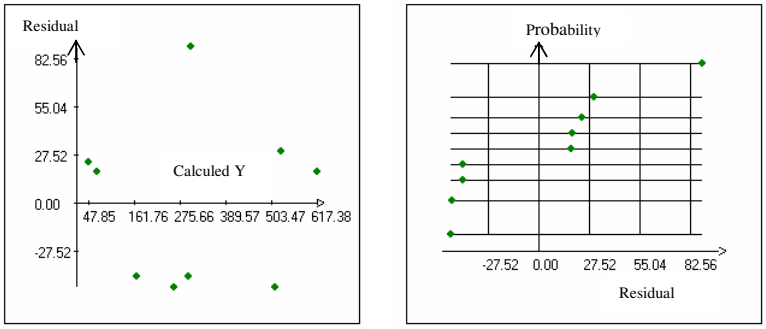

Fig.1. Study of the residuals of the response $\hat{Y}_1$.

(a) residual versus responses (b) normal probability plot of residuals

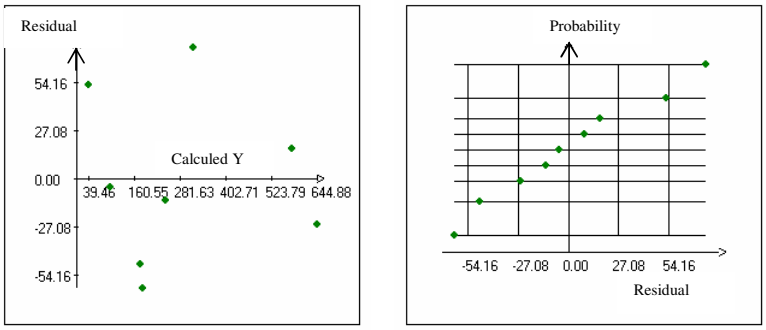

Fig. 2. Study of the residuals of the response $\hat{Y}_2$.

(a) residual versus responses (b) normal probability plot of residuals

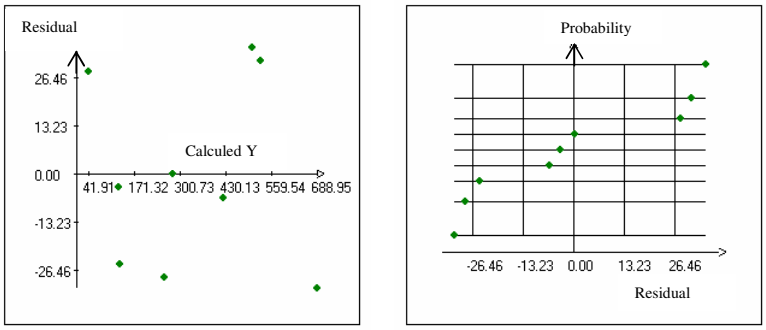

Fig. 3. Study of the residuals of the response $\hat{Y}_3$.

The Henry lines (Fig. 1b, 2b and 3b) conclude that the residues follow a normal distribution; almost points are aligned in a gausso-arithmetic graph.

The complete analysis of variance was summarized in Table 5. The statistical test allowed us to conclude that the main effect of the pH was the most significant factor on the specific surface response for the three studied cases.

Table 5. Significance of effects by analysis of variance for $\hat{Y}_1$, $\hat{Y}_2$ and $\hat{Y}_3$.

Responses	Main and interactions effects	Coefficient	Standard deviation	t.exp.	Signif. %
$\hat{Y}_1$	b_0	260.620	58.037	4.49	1.90 *
	b_1	-228.507	31.788	-7.19	0.440 **
	b_2	-3.187	31.788	-0.10	92.4
	b_{11}	37.360	55.058	0.68	54.8
	b_{22}	37.820	55.058	0.69	54.4
	b_{12}	-56.255	38.932	-1.44	24.4
$\hat{Y}_2$	b_0	183.894	53.657	3.43	4.02 *
	b_1	-237.148	29.389	-8.07	0.302 **
	b_2	-36.685	29.389	-1.25	30.1
	b_{11}	92.718	50.903	1.82	16.5
	b_{22}	97.108	50.903	1.91	15.2
	b_{12}	-2.677	35.994	-0.07	94.4
$\hat{Y}_3$	b_0	424.540	31.682	13.40	0.0578 ***
	b_1	-199.443	17.353	-11.49	0.0946 ***
	b_2	-124.077	17.353	-7.15	0.448 **
	b_{11}	-96.310	30.056	-3.20	4.78 *
	b_{22}	-43.710	30.056	-1.45	24.2
	b_{12}	80.910	21.253	3.81	3.03 *

* Significant with a confidence degree of 95 %
** Significant with a confidence degree of 99 %
*** Significant with a confidence degree of 99.9 %

3.2. Interpretation of the response surface models

The relationship between the responses and the experimental variables could be illustrated graphically by plotting both the response values versus the levels of variables simultaneously. The topography of these three-dimensional response surfaces also could be illustrated by isoresponse contour lines (Fig. 4b, 5b and 6b), which represented curves of constant response on a two-variable plan (fig. 4a, 5a and6a). Such plots were helpful in studying the effects of the variation of the factors in the domain studied and, consequently, in determining the optimal

experimental conditions. In the case of methanol, the pH effect is negative (b_1 = - 228.507) and it is more significant than that of the concentration (b_2 = -3.187). Best specific surface areas are obtained with pH acids and low silica concentrations. The interaction coefficient between pH and silica concentration (b_{12} = - 56.255) and the translating coefficients nonlinear influence of these variables (b_{11} = 37.360; b_{22} = 37.820) are weak: their influences on specific surface area are negligible.

Using ethanol, pH remains always the most influential factor compared to the concentration (b_1 = - 237.148; b_2 = - 36.685). The interaction between the two factors is negligible (b_{12} = - 2.677) and the nonlinear influences of pH and the concentration (b_{11} = 92.718; b_{22} = 97.108) is weak. With weak pH and low silica concentrations, specific surface areas are very important.

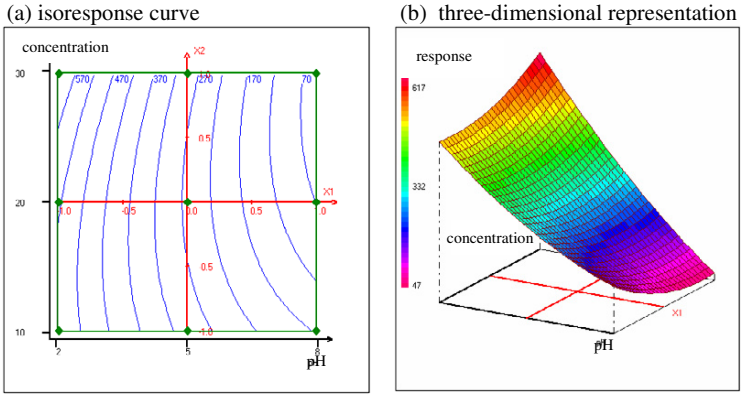

Fig. 4. Specific surface area variation (Y) according to pH (X_1) and the concentration (X_2) in presence of methanol.

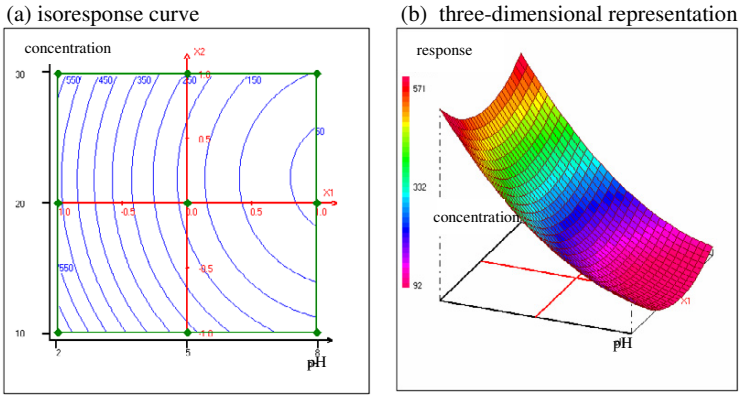

Fig. 5. Specific surface area variation (Y) according to pH (X_1) and the concentration (X_2) in presence of ethanol.

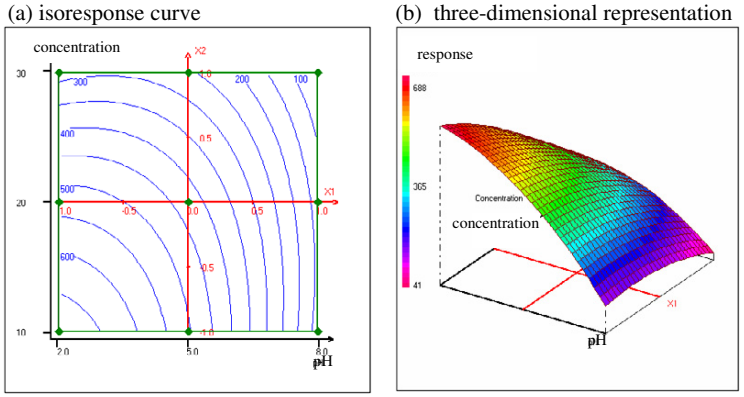

Fig. 6. Specific surface area variation (Y) according to pH (X_1) and the concentration (X_2) without alcohol.

Without alcohol, the effects of pH and the concentration are comparable (b_1 = - 199.443; b_2 = - 124.077). They are more significant than their interaction (b_{12} = 80.910).

3.3. Optimization

The objective of this work is to determine the experimental conditions which are adequate for the silica gel, starting from Tunisian sand, convenient as adsorbing in order to eliminate the polluting entities in a phase of liquid or gaz. Through using the methodology of experimental design, the pH fields and the silica concentration have been determined in order to obtain a silica gel having a specific surface area deemed important. The elaborated models are made the most of silica gel. This is done to have a digital research of the optimal conditions of the silica gel preparation. The functions of "Desirability" of NERMOND software are resorted. The results are presented in table 6.

Table 6. Optima coordinated

		methanol	**ethanol**	**Without alcohol**
pH		2	2	2
Concentration	($g.L^{-1}$)	30	10	10
Specific surface area	($m^2.g^{-1}$)			
- theoretical		621.69	647.35	689.00
- experimental		635.20	619.00	657.60

Prepared silica gel presents rather porous textures, what is translated by important specific surfaces of the order of 650 $m^2.g^{-1}$. The manufacturing of the silica gel in pH acid (pH = 2) gives the best specific surface whatever is the used concentration. The gel prepared without alcohol, is the most adequate gel, indeed it has the highest specific surface area, it can low be of industrial interest by its production cost because it requires a weak silica concentration what results in small quantities of sand.

4. CONCLUSIONS

The preparation of a silica gel from Tunisian sand presenting a high specific surface was the object of this work. Silica gels were obtained from sodium silicate solution mixed with hydrochloric acid by sol-gel process. Preparation of silica gels depends on several factors. Three parameters are held: Precursor concentration (sodium silicate), pH and the additives (methanol, ethanol).

An experiment matrix of Hoke D6 was used in order to minimize the number of experiments to be realized. Specific surface area represents the response of each gel prepared in all the studied experimental fields. The analysis

of variance of all the responses gave the coefficient R^2 to be higher than 95 % suggesting that the model is a good fit.

Factorial designs (three variables - three levels) were chosen as the experimental designs. The results obtained after measuring the specific surface area were fitted as a three-variable second order equation and the corresponding contour plots were plotted and analysed. The optimum silica gel having an important specific surface area (657.60 $m^2.g^{-1}$). This gel is obtained by using pH acid (pH = 2) whatever the concentration used. It also proved that this silica gel obtained without alcohol.

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